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PRODUCTION OF POLYMER / FOOD GRADE SOLVENTS FROM PARAFFIN RICH LOW VALUE STREAMS EMPLOYING HYDROPROCESSING

FIELD OF THE INVENTION

The present invention relates to the process for the preparation of Polymer/ Food grade hydrocarbon solvents of naphtha range essentially free from olefins less than 20 ppm of aromatics and less than 1 ppm of sulfur from paraffinic-rich low value streams such as raffinate from the solvent extraction units in crude oil refineries employed for recovery of aromatics from reformat by hydrogenation in the presence of a nickel based catalyst.

BACKGROUND OF THE INVENTION

Petroleum naphtha is a widely used solvent both in industry and laboratories. Different grades of naphtha solvents are available for various applications. These solvents are normally used as

- a) an ingredient in the finished product,
- b) solvents for extraction of vegetable oil (from oil seeds), minerals, pharmaceuticals,
- c) solvents for reactants e.g. in polymerization reactor and
- d) solvents for cleanup and maintenance operations.

These solvents are manufactured from low boiling refinery streams like naphtha and find their applications in agriculture, food and pharmaceuticals, petrochemicals, printing, paint and coating, chemical industries etc.

Though, there does not exist any universally accepted nomenclature for hydrocarbon solvents, most manufacturers group their solvents according to boiling point and composition. Distillation range is also one of the main criteria. Solvent grades with narrow and wide boiling ranges, also referred to as " Special Boiling Point Spirits " (SBPS) are generally found in the boiling range of 45-160° C. White spirit is the name given to solvents in the boiling range-of 150 - 220° C. Composition is another important parameter for characterizing the solvents. Depending upon the type of compounds present in the solvents, they are named such as aromatic solvents, Isoparaffinic solvents. For most of the polymers and resins, solvent power is found in the following order:

Aromatics > Napthenes > n-Paraffins > i-Paraffins

Aromatics are known to have maximum solubilizing power. However, from toxicological and performance point of view, benzene-free and very low aromatic content solvents are required in applications e.g. Oil seed extraction, polyolefins manufacture, printing inks and adhesives.

Evaporation rate, appearance, color and odor are some of the other important characteristics of solvents. When the solvents consist mainly of a single hydrocarbon, they are named after the same e.g. Hexane, Isohexane, Heptane etc.

In an extraction processes, the function of the solvent is to extract selectively some particular ingredient from a mixed product or raw material e.g. vegetable oils, pharmaceuticals, cleaning & degreasing etc. For food processing and pharmaceutical applications, criteria must be strictly qualified with respect to present of compounds having toxicological properties. In chemical process, the function of the solvent is to act as an inert reaction medium or catalyst carrier e.g. in polyolefins manufacture. In these and other process, apart from benzene and other aromatics content, strict specifications are maintained with respect to olefins, Sulfur also.

The product from Hydrocracking unit are very low in aromatics. Therefore, fractionation of hydrocracker naphtha into suitable boiling ranges is often done to produce dearomatised solvents. But hydrocracker naphtha is a premium product and has other preferred uses e.g. feedstock for reforming, ethylene cracking etc. The 'S' content in Hydrocracker naphtha quite often exceeds 1 ppm due to recombination of H_2S and olefins into mercaptans. This amount of sulfur is unacceptable in Food Grade and Polymer Grade solvents. Catalytic hydrogenation of Straight Run Naphtha streams is another option. However, the sulfur present in these streams require prior desulfurisation and the higher pressure process employing sulfided catalysts are uneconomical. Patents describe processes for hydrogenation of benzene in heterogeneous reactor either in liquid phase (US 4327234 : Hydrogenation process using supported nickel catalyst) or in gas phase (US 577186 : Process for hydrogenating benzene in hydrocarbon oils) as well as in homogeneous reactor (US 5668293 : Catalyst and a benzene hydrogenation process using said catalyst). Patents also describe processes for benzene hydrogenation through catalytic distillation (US 6084141 : Hydrogenation process comprising a catalytic distillation zone comprising a reaction zone with distribution of hydrogen, US 6048450 : Process for the selective reduction to the content of benzene and light unsaturated compounds in a hydrocarbon cut). However, all these processes are meant for meeting benzene specifications in MS where benzene is required to be reduced to 1 vol % only to meet the most stringent Euro-IV standard. In addition to hydrogenation of benzene in fuels, patents describe processes for production of cyclohexane also through hydrogenation of Benzene (US 5589600 : Preparation of cyclohexene by partial hydrogenation of benzene).

Solvent extraction is another method used for the production of dearomatised solvents. A patent (IN 168536) describes such a process of Separation of benzene and C5-6 non-aromatic hydrocarbons from naphtha fractions by countercurrent extraction for recovery of food-grade n-hexane.

However, for very low aromatics concentration in solvents, solvent extraction would be prohibitively expensive. Moreover, solvent extracted paraffins have relatively lower solvent power in comparison to hydrogenated solvents, as the naphthenes from saturation partly compensate for the solvent power of the aromatics. Moreover, solvent extracted solvents may not be able to meet the specifications for Bromine member (olefins).

Adsorptive dearomatisation using silica gel, alumina and activated carbon has not so far been attractive for large scale commercial production due to requirements for continuous regeneration. Acidic clays also been used for production of solvents. But they only remove olefins, not aromatics. Two patents (IN 184574 & IN 179409) describe methods to produce Food Grade Hexane through adsorption and clay treatment.

SUMMARY OF THE INVENTION

The present invention generally relates to a catalytic hydrogenation process for the preparation of polymer / food grade hydrocarbon solvents in naphtha range essentially free from olefins and having aromatics less than 20 ppm and sulfur less than 1 ppm nil olefins from naphtha range petroleum stock and more preferably from raffinate obtained from BTX extraction unit, e.g. Udex, using a Nickel based catalyst.

DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to a catalytic hydrogenation process for the preparation of polymer / food grade hydrocarbon solvents of naphtha range containing very low aromatics, especially benzene less than 20ppm from naphtha range petroleum stock. More particularly, the present invention relates to a catalytic hydrogenation process for the preparation of polymer / food grade hydrocarbon solvents of naphtha range essentially free of olefins, containing aromatics less than 10 ppm and containing sulfur less than 1 ppm from paraffinic rich solvents which are substantially free from Sulfur, chlorides.

The present invention provides a process for preparing polymer/food grade hydrocarbon solvents of naphtha range containing very low aromatics, especially benzene less than 20ppm from naphtha range petroleum stock, said process comprising:

- a. heating the naphtha range petroleum feed to a temperature in the range of 70° –180° C;
- b. adding stoichiometric amount of hydrogen to the naphtha range petroleum feed at a pressure between about 5 to 30 bar;
- c. passing the mixture of feed and hydrogen through a reactor having a nickel based catalyst, and
- d. removing any excess hydrogen to obtain polymer/food grade hydrocarbon solvents of naphtha range containing very low aromatics.

In an embodiment of the present invention, the naphtha range petroleum feed is preferably raffinate from the solvent extraction units employed for recovery of aromatics from reformat.

In another embodiment of the present invention, the raffinate feed has sulfur < 50ppm, preferably < 5ppm and most preferably <1ppm.

In yet another embodiment of the present invention, the raffinate feed has aromatics < 20% by wt and preferably <10% by wt.

In still another embodiment of the present invention, the raffinate feed has benzene < 20% by wt and preferably <10% by wt.

In a further embodiment of the present invention, the raffinate feed has boiling point in the range of C₅ to 110°C.

In one more embodiment of the present invention, the raffinate feed has boiling point in the range of 63°-70°C.

In one another embodiment of the present invention, the raffinate stream has about 4 to 7% by wt benzene.

In an embodiment of the present invention, the catalyst is nickel supported on alumina catalyst.

In another embodiment of the present invention, the nickel loading is about 10 to 70% by wt. and preferably is about 30 to 60% by wt.

In still another embodiment of the present invention, the metal surface area of the nickel-alumina catalyst is about 10-20 m²/g.

In yet another embodiment of the present invention, the physical surface area of the nickel-alumina catalyst is about 120-200 m²/g and the pore volume of the catalyst is about 0.2-0.3.

Feed: The feed is of naphtha range having boiling range of C₅ - 110° C. In particular, the feed should have boiling point in the range of 63°-70° C for producing Food/Polymer grade hexane. The feed should be substantially free from Sulfur i.e. the sulfur content in the feed should be <50

ppm), more preferably <5 ppm and most preferably <1 ppm. The amount of the aromatics in the feed should be < 20% and more preferably less than 10%. The Applicants have found that Raffinates of BTX extraction column post reforming make excellent feed stock qualifying the necessary feed properties. In a most preferred embodiment of the present invention, Udex raffinate having a boiling point of 63°-70° C is used for the production of Food /Polymer grade Hexane substantially free of benzene and aromatics.

In the present invention, the feed is reacted with Hydrogen in presence of a catalyst at a temperature range of 70-180°C and under a pressure of 10 to 30 bars. The reaction is carried out preferably in a three phase reactor and more preferably the reaction is conducted in a tubular fixed bed reactor and most preferably, in a down flow Trickle Bed Reactor.

Catalyst: In the present invention, Metals of Group VIII supported on inert material are used to catalyze the hydrogenation reaction. More particularly, nickel supported on alumina is a preferred catalyst. Nickel loading is from 10-70 wt% and more preferably from 30-60 wt%. The metal surface area is between 10-20 m²/g. The physical surface area of the support material after impregnation of Nickel is between 120-200 m²/g. The pore volume of the catalyst is between 0.2-0.3 cc/gm. The crushing strength of the catalyst is above 1 MPa. Nickel Oxide on the catalyst is reduced to its active form Ni in the reactor at 380°C - 420°C with Hydrogen. In another preferred embodiment, the catalyst is reduced ex-situ and then exposed to a mixture of 1-4% O₂ to give a coating of inert oxide on the active catalyst for safe handling. After loading in the reactor under inert nitrogen, the outer inert oxidized layer is reduced at 160°C - 200°C under hydrogen flow rate.

In this process Feed is heated to the reaction temperature which is between 70-180°C, and preferably between 80-150°C. Hydrogen is mixed with Feed at the pressure between 5 to 30 bar and more preferably between 10 to 20 bar. Hydrogenation reaction takes place in the reactor on the active sites of catalyst under operating conditions as described above. The product coming out of the reactor is separated from unreacted Hydrogen in a separator. Very little hydrogen is introduced in excess to the stoichiometric amount to the reactor. As a result, there is no need for recycle of un-reacted Hydrogen. In one embodiment of the process, a bed of sulfur guard adsorbents is placed in the reactor before catalyst when 'S' level in feed is higher than 5 ppm. In another embodiment of the process, a bed of chloride guard adsorbents are placed in the reactor before catalyst when 'Cl' level in feed is higher than 1 ppm.

In another embodiment of the process, a dryer of Molecular Sieve is placed before the reactor. When moisture in feed is higher than 1 ppm. Product from the reactor is hydrocarbon stream of same boiling range as that of Feed and substantially free from Aromatics, more particularly, Benzene.

The invention will be further illustrated by the following examples. While the Examples are provided to illustrate the present invention, they are not intended to limit it.

Example – 1:

The raffinate streams of a reformat extraction unit has the following composition:

Component	% wt
2,3 dienethyl Butane	4.1
2 Methyl Pertane	18.7
3 Methyl Pertane	15.0
N – Hexane	23.4
Methyl Cyclopertane	4.5
Benzene	7.2
Methyl Hexane	13.2
N Heptane	7.4
Tolune	6.5

This was fed along with hydrogen to a tubular reactor having catalyst of following properties.

Catalyst characteristics

Chemical composition	NiO ₂ /Al ₂ O ₃
Physical Surface area	162 m ² /gm
Pore volume	0.221 cc/gm
Av. Pore diameter	55 A ⁰
Bulk Crushing strength	1.96 Mpa
Metal Surface Area	14.82 m ² /gm
Metal dispersion	5.6%

The catalyst was activated under H₂ flow at atmospheric pressure and 400⁰C to reduce the oxidized Nickel to Ni.

The results of the runs are as following properties:

Run No. 1	LHV in hr ⁻¹	Temperature in °C	Pressure Kg/cm ² g	Aromatics in products	
				Benzene	Tolune
1.	4.0	100	30	50ppm	ND
2.	4.0	140	20	30ppm	ND
3.	4.0	120	15	60ppm	ND
4.	2.0	100	15	72ppm	ND
5.	2.0	120	20	45ppm	ND

ND : Not detected

Example - 2

A heart cut was prepared from a Naphtha stream from the raffinate of a Udex unit and this was hydrotreated in a Trickle Bed Reactor.

The catalyst properties are as following :

Catalyst Characteristics

Chemical composition	NiO ₂ /Al ₂ O ₃
Ni Content	40%
Metal surface area	20 m ² /gm
Physical surface area	170 m ² /gm
Crushing strength	1.3 Mpa

The catalyst was pre-reduced under Hydrogen and then a thin oxide layer was formed by exposed the catalyst to a mixture of 1% O₂. After loading the catalyst into the reactor, it was reduced at 180°C with Hydrogen.

The operating condition of the run are as follows

Feed space velocity, hr ⁻¹ .	1.3
Inlet Temperature, °C	95
Pressure, kg/cm ² g	18
H ₂ flow rate, Nm ³ /m ³ of feed	28.5

The feed and Product composition are as follows:

S.No.	Component	% wt/wt	
		Feed	Product
1.	2,2 Dimethyl butane		
2.	Cyclopentane 2,3 DiMethyl butane	1.00	1.06
3.	2 Methyl pentane	9.73	10.98
4.	3 Methyl pentane	21.14	25.84
5.	n-Hexane	53.56	52.90
6.	Trans-2-hexene-	0.35	-
7.	2- Methyl pentene-2	0.49	-
8.	4-Methyl pentene-2	0.33	-
9.	Cis-2-hexane	0.18	-
10.	3 Methyl pentene-2	0.50	-
11.	2,2 DiMethyl pentane	0.25	-
12.	Methyl cyclopentane	7.48	5.68
13.	2,4 DiMethyl pentane	0.36	-
14.	Benzene	4.02	ND*
15.	3,3 DiMethyl pentane	0.04	-
16.	Cyclohexane	0.29	3.54
17.	2-Methyl hexane	0.13	-
18.	2,3 DiMethyl pentane	0.05	-
19.	3-Methyl hexane	0.10	-
	ND (Not detected) * : Less than 20 ppm	100.0	100.00